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A study of the possible formation of a mixed hydrogel of zirconia and silica

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A STUDY OF THE POSSIBLE FORMATION OF A MIXED HYDROGEL OF ZIRCONIA AND SILICA

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INTRODUCTION

It has been known for sometime that a hydrogel is formed when an acid is added to a solution of sodium silicate, and also when a base is added to a solution of a zirconium salt, for example $ZrOCl_2$, known as zirconyl chloride or zirconium oxychloride. The properties of the hydrated silica gel have been investigated thoroughly in this laboratory over a period of some ten or fifteen years, while work on the hydrated zirconia gel was initiated by Fallon[1] in 1938. Attention has been paid especially to the effect which various factors had, such as temperature, pH, presence of electrolytes and many others, on the time of set of the gel.

Although the properties of the zirconia hydrogel have not been studied so extensively as those of the silica, there have been compiled a fair amount of significant data which have been published.

A logical outcome of the work on these two gels which led to the start of this new phase of work which this paper covers has been the thought that if the basic sodium silicate should be added to the acidic zirconyl chloride, a gel would be formed which might very well be a mixed gel or co-gel, a study of whose properties might prove interesting indeed. The thought which prompted this investigation

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1. Refer to corresponding number in bibliography. All succeeding reference numbers refer to bibliography.

was certainly logical enough. It was impossible, of course, to foresee the many obstacles which beset this work before any gel could even be prepared.

The purpose of this research has been to determine the conditions necessary for the formation of a co-gel of hydrated silica and zirconia in the hopes of initiating the investigation of the properties and charateristics of such a gel. Success in this endeavor was seriously hampered by the very persistent gelatinous precipitate which fell out immediately upon mixing the two solutions. This problem was not resolved for the major part of the time in which research was possible, and for the rest of the time other obstacles arose which will be described in the succeeding pages. Nevertheless some valuable experience was gained and some valuable suggestions can be given as a result of this work which may be of aid to future workers in the field.

Perhaps it would be wise in considering a new subject of this kind to review briefly the chemistry of the zirconium and silicon compounds encountered in this work. A complete review of zirconium compounds may be found in Venable's[10] book on the subject or in Mellor's[5] treatise. As far as the silicon compounds are concerned, the great volume of work done on this subject in this laboratory provides a good source.

Considering zirconium first --- when ammonia or any

alkali hydroxide is added to a solution of a zirconyl salt, a voluminous gelatinous precipitate is obtained. If done in the cold, this precipitate is regarded as $Zr(OH)_4$, the ortho form. When precipitation occurs from a hot solution, $ZrO(OH)_2$, the meta form is assumed. The hydroxides are virtually insoluble in water, the ortho is soluble in acid readily, the meta slowly, but eventually to the same degree as the ortho.

The hydroxide is amphoteric. Zirconyl salts are formed with strong acids, and salts of the acid H_2ZrO_3 are precipitated by strong bases, although the existence of this meta acid is not confirmed.

Zirconium oxychloride, the compound used in this investigation is a typical salt. It may be formed by dissolving the hydroxide in dilute hydrochloric acid, but is only slightly soluble in concentrated acid. The normal hydrate contains eight molecules of water, but the literature reports many more basic hydrates (Meller)[5].

The hydrolysis of zirconium oxychloride has been investigated by Pauli[6], who concluded that simple ionization is negligible in a solution of this salt. Freshly prepared solutions undergo continuous hydrolysis for about three days and remain practically constant after that over a period of six months. It proceeds to about 35 to 50% and doesnot increase with dilution; the solutions remain per-

fectly clear.

The curves for H^+ and Cl^- concentrations versus concentration of $ZrOCl_2$ are S- shaped so that at very low and again at moderate concentrations, the H^+ is greater than the Cl^- concentration, indicating the presence of complex ions containing the zirconium. The fraction of total chloride existing as free Cl^- varies irregularly with the concentration, the curve exhibiting two maxima. Pauli's conclusions drawn from conductance measurements indicate that a large part of the conductance is due to the complexes, which vary irregularly with the $ZrOCl_2$ concentration.

Typical complexes assumed by Pauli are:

CATIONS

$Zr(OH)_4 \cdot ZrO$ $+ +$

$Zr(OH)_4 \cdot ZrOCl_2 \cdot ZrO$ $+ +$

ANIONS

$Zr(OH)_4 Cl_2$ $- -$

$Zr(OH)_2 Cl_4$ $- -$

When the positive and negative zirconium complex ions are equal in numbers, coagulation results.

Hurd, Fallon, and Hobday[3] have prepared gels of hydrated zirconia in this laboratory by several different methods, including the addition of sodium carbonate to zirconium oxychloride solution, and also by the addition

of sodium acetate. Prakash[7] earlier made gels of hydrated zirconia by the addition of NaOAc to zirconium nitrate solutions. He also reports clear, hard, transparent gels from a dialysis of a mixture of zirconium nitrate and potassium molybdate.

Of course in this paper we are also interested in the gel of hydrated silica, which has been studied here thoroughly for several years. A discussion of the theory and work on this subject would take up too much time and space, since this field has been much more widely studied than any other in the field of gels. Reference to Hurd's "Theories for the Mechanism of the Setting of Silicic Acid Gels"[2] presents a complete summary of the theory behind the setting of this gel.

EXPERIMENTAL

First, of course, the solutions had to be prepared. For the zirconium, the same salt was used as has been found the most suitable by Hurd, Fallon, and Hobday[3], that is, zirconium oxychloride, obtained from the Titanium Alloy Manufacturing Company, Niagara Falls, New York. The analysis of the zirconium oxychloride is as follows: ZrO_2, 40%; Cl, 22%; Fe, .05%; Ti, .05%. The rest, of course, is water of crystallization. The standard solution used

throughout was made from 385 grams of the salt per liter of solution. The solution used, not made up quantitatively, was titrated with 1.242 normal sodium hydroxide, and found to contain .947 moles of ZrO_2 per liter. Of course actually, the H_2SO_4 equivalent was titrated, and the ZrO_2 concentration was calculated from it.

The silicate solution was prepared from the usual "E" brand silicate, or water glass, specific gravity 1.383. The solution was first prepared by diluting 2 liters of the water glass to 14 liters of solution. This solution was later found to be weaker than the 1.3 normal solution which has been used in the past, and was concentrated by adding more water glass until a 1.278 normal solution with respect to sodium hydroxide was obtained, or in other words, one containing 2.096 moles of SiO_2 per liter.

Rough trials to initiate the experimental work immediately showed up what was to prove the greatest nuisance during the entire year's work. That is, in mixing small portions of each of the standard solutions together, a voluminous, gelatinous precipitate immediately fell out.

With this problem in view, a systematic attempt at using many different proportions and concentrations of each component was attempted in the hope of preventing the precipitation. Finally, concentrations were steadily diminished until such great dilutions were ultimately used that it is doubtful if a

gel could possibly form from them.

During this period of cut-and-try experimenting it was found that if the zirconium oxychloride solution were added to the sodium silicate solution a precipitate formed immediately no matter what the respective concentrations. In the case of addition of sodium silicate to the zirconium oxychloride on the other hand, it was found that in the more acid solutions, with constant electric motor-driven stirring, the precipitate could be made to dissolve. At the very low pH at which this was possible, however, gels were not formed over even a long period of time. This experiment also showed the basic properties of the precipitate and indicated that the compound was probably one of zirconium. In fact, all indications point to the fact that the precipitate was zirconium hydroxide, $Zr(OH)_4$, sometimes written as orthozirconic acid, H_4ZrO_4, since, according to Venable[10], it is amphoteric.

Working on that basis it was deemed worthwhile to attempt the following: If the sodium silicate solution should be added to the $ZrOCl_2$ solution making quite an acid solution so that all the precipitate remained in solution, a solution of sodium acetate added slowly might bring up the pH to a point where co-gelation might occur.

An approximately 1.5 normal solution of sodium acetate was therefore prepared by adding 82 grams of the salt, diluting to a liter of solution.

The above mentioned experiments were also tried by making the zirconium oxychloride solution more acidic with a 2 normal acetic acid solution.

The mixtures tried and the results obtained are tabulated in Table I on page IX.

The values of pH of these solutions would obviously have been important since the proportions of ZrO_2 and SiO_2 do not alone determine the effect on the physical appearance of the gel when the mixture contains the other components. Unfortunately, however, the pH was not recorded in this set of data. There is obviously a large excess of SiO_2 over ZrO_2 in each of the mixtures, and yet gel number 4 resembles a hydrated zirconia gel.

An interesting fact in these data occurs in gel number 4 which set as a gel of hydrated zirconia, that is, a white soft gel, exhibiting marked syneresis properties. The next day, however, the gel appeared harder and firmer, and vibrated, possibly indicating that the hydrated silicic acid gel set later. Of course, the above postulations as to the structure of the gels are merely suggested as possibilities. They are not verified on the basis of scientific investigation.

In another set of data, the determination of the variation in time of set with change in pH, that is by changing the amount of sodium acetate in the mixture keeping other things constant was attempted.

TABLE I.

	Volume of $ZrOCl_2$	Volume of Na_2SiO_3	Results
1.	5 cc of standard 5 cc of 2N HAc 5 cc of H_2O	5 cc of new standard 15 cc of H_2O	Hard, firm gel set in two days. Resembles silicic acid gel.
	Mixture contains .135 moles ZrO_2 per liter and .30 moles SiO_2 per liter.		
2.	10 cc of standard 10 cc of H_2O	10 cc of new standard 5 cc of H_2O 5 cc of 2N HAc	Precipitate and a gel in two days, resembles silicic acid gel.
	Mixture contains .237 moles ZrO_2 per liter and .524 moles SiO_2 per liter.		
3.	10 cc of standard 10 cc of H_2O 10 cc of 2N HAc	12 cc of new standard 10 cc of H_2O	Gel in two days, resembles (1) and (2).
	Mixture contains .182 moles ZrO_2 per liter and .483 moles SiO_2 per liter.		
4.	10 cc of standard 10 cc of 2N HAc 10 cc of H_2O	10 cc of new standard 10 cc of H_2O	Set rapidly, resembles hydrated zirconia gel.
	Mix and add 5.5 cc of 1.5N HAc.		
	Mixture contains .171 moles ZrO_2 per liter and .420 moles SiO_2 per liter.		

These mixtures were kept at a constant temperature of 25° C. in a thermostatically controlled water bath operated by a mercury-toluene thermo-regulator in a mercury thyratron tube control circuit. The pH was determined, using a Leeds-Northrup quinhydrone potentiometer and a one normal calomel cell with a bright platinum electrode.

In this set of data and as discovered in subsequent runs, it was found very difficult, if not impossible to control the pH and time of set within reasonable values and with reproducible results. This difficulty was no doubt a result of the rather unbuffered solutions which were used throughout (though the sodium acetate must have had some buffer action), so that a slight change in the amount of a certain component added, for example sodium acetate, would have a very marked effect on the time of set.

One set of data did show the general trend of the time of set and the change in appearance of the various gels with variation in the amount of sodium acetate added. This was done as carefully as possible at 25° C. The sodium acetate was added from a burette which was immersed in the thermostated bath when not in use.

All mixtures contained 10 cc of zirconyl chloride, 10 cc of two normal acetic acid, and 10 cc of the sodium silicate solution with varying amounts of sodium acetate

in a total volume of 50 cc.

TABLE II

Gel Number	Volume H_2O Added	Volume 1.5N NaAc Added	pH	Time of Set
1	19 cc	1 cc	.60	overnight (?)
2	17 cc	3 cc	.60	overnight (?)
3	16 cc	4 cc	1.57	100 minutes
4	15.5 cc	4.5 cc	2.09	19 minutes
5	15 cc	5.cc	2.09	8 minutes

Gel numbers 1 and 2 set overnight, and resembled silica gels, that is clear transparent vibrant gels. Their very low values of pH seem to bear this out. Gels 4 and 5 set comparatively rapidly, and resembled the zirconia gel described by Hurd, Fallon and Hobday[3], that is the rather opaque, synerizing, non-vibrant gel. Its pH, which is 2.09 lies in the region favorable for zirconia gel setting, namely 2.0 to 5.0. Gel number 3. is more interesting, setting at an intermediate time with a pH below the region for zirconia gels, as shown by Hurd, Fallon, and Hobday[3], and yet resembling the zirconia gel in its opacity, and the silica gel in its elasticity. The possibility of a co-gelling mixture does not seem unreal at this point. Yet as stated above, results in this phase of the work are very difficult, if

not impossible to reproduce regularly. A very promising problem for future research would be to investigate this phase of the work in an effort to devise a method yielding more reproducible results.

Beset by these many difficulties, it was thought that more immediate results might be obtained if some method of prevention of precipitation of the zirconium hydroxide could be found, such as a peptizing agent or some other such substance. A search of the literature produced two possibilities.

Mellor[5] in his section on zirconium, states, "Unlike yttrium hydroxide, the precipitation of zirconium hydroxide is prevented if tartaric acid be present." This might be expected since some metals do form soluble complex tartrates. Various amounts of tartaric acid were added to the zirconium oxychloride solution before the addition of the silicate, but no visible amount of peptization or prevention of precipitation occurred. Checking on Mellor's statement above which implies that the precipitation of yttrium hydroxide is not prevented, it was found in his section on yttrium that "if tartaric, citric or other oxy-acid is present, no hydroxide is precipitated". Evidently, then, there must have been a typographical error in the first case; no further time was spent on this supposed possibility.

The second possibility seemed to present something a

bit more promising. K. C. Sen[8] found it possible to prevent the precipitation of certain metal hydroxides by means of sugars. He found that cane sugar caused peptization of the hydroxides of Zr, La, Y, and U, when their precipitation from solution by alkalies is attempted. Lactose and dextrose were effective with Zr and U, and levulose caused peptization with Zr, U, and Y.

Although Sen claimed levulose was the most effective for zirconium, with dextrose second, dextrose was used because it is so much cheaper in price.

Sen[9] advances the following theory for the so-called peptization of precipitates by non-electrolytes like sugar or glycerol: non-electrolytes do not actually peptize a precipitate. Their disintegrating action, if any, is small. The mechanism of their action lies in the fact that when they are present in the solution, they are adsorbed by the precipitating particles and thus prevent the growth of crystals. In other words, due to this surface film, coalescence is to a certain extent prevented and the precipitating substance is stabilized by the preferential adsorption of some ions present in the solution. Simply stated, the action is one of protection, rather than peptization, according to Sen.

Using dextrose, then, the experimental work was marked after long last by the production of the first hydrogel from

zirconium oxychloride and sodium silicate solutions done without the addition of any other electrolytes of any kind. The first gel was made by merely adding the standard sodium silicate solution to 10 cc of the zirconium oxychloride solution to which 5 grams of dextrose had been added until peptization ceased. In two days, a clear gel was found which, when tested by the "tilted rod" method[4], broke open at the surface in a manner not characteristic of the pure silicic acid gel. This characteristic has been noted, however, by Fallon[1], in his work on the pure hydrated zirconia gel. He suggests as an explanation for this, capillary evaporation at the surface. The fact that this phenomenon was observed in the pure zirconia gel may indicate that the gel mentioned above was just that. However the mixture did contain a higher concentration of silica than zirconia.

Although on the basis of what was supposed to be careful investigation, it was thought that dextrose actually peptized the precipitate to an appreciable extent, later more exacting runs showed it to be essentially ineffective. In other words, the same results could be obtained without dextrose. All that was necessary to prevent precipitation up to a point was to dilute the sodium silicate solution greatly and add the diluted solution to the standard zirconium oxychloride. Sen's previously mentioned paper on peptization apparently was concerned with very small volumes and fairly

large amounts of dextrose. It does not seem to hold for the volumes used in this work.

Be that as it may, the data obtained with dextrose may be recorded neglecting the dextrose, since Sen[8] says that the dextrose has no effect on the properties of the solution, although it did produce a yellow coloration.

It was found that if 10 cc of Na_2SiO_3 solution was diluted to 70 cc and then added to 10 cc of the standard $ZrOCl_2$ solution, a clear soft gel would set in about 10 hours. A mixture of this kind contains .262 gram moles of SiO_2 per liter and .119 gram moles of ZrO_2 per liter, obviously a decided excess of silica. In order to avoid this excess of silica, 120 grams of NaOH pellets were added to a liter of the original sodium silicate solution in order to make the normality with respect to sodium hydroxide equivalent to the concentration of the silica.

Now taking 5 cc of this new silicate solution, and diluting to 70 cc, when four-fifths of this solution had been added to the 10 cc of zirconyl chloride, the gel had set. This gel was another resembling the hydrated zirconia. Synersis took place around the entire gel, so that the gel was practically floating in the exuded liquid. An interesting point is shown here. According to Hurd, Fallon and Hobday[3], hydrated zirconia gels which have set in a comparatively short time reliquefy in a few hours. None of

the gels made by the above method, although resembling zirconia gels, reliquefied upon standing. This may be another piece of evidence for the existence of the co-gel.

In order to compare the properties of a pure zirconia gel with what might possibly be a mixed gel, a solution of sodium hydroxide was prepared which, upon analysis, proved to have the same normality as the silicate solution with respect to sodium hydroxide, namely, 1.278 normal. 15 cc of this solution was diluted to 70 cc. 50 cc of this new solution was added to 10 cc of the zirconyl chloride solution, and a soft, inelastic zirconia gel was formed. The same volume of a similarly prepared silicate solution was added to 10 cc of the zirconyl chloride solution. The resultant gel was elastic, but it showed a peculiar property--- that after it was apparently set, a glass rod placed in the gel broke the surface and split the inside. In other words, the gel does not have the firm, cohesive body of the silica gel and yet is much firmer than the zirconia gel.

The zirconia in this gel seems to modify the properties of the silica gel, whereas in previously described experiments, the silica seemed to be modifying the characteristics of the zirconia gel. As an hypothesis, one might postulate that the zirconium in a gel tends to destroy the structure of the usually stable silica gel, whereas the

silica tends to strengthen the structure of the usually weakly constructed zirconia gel, these two opposing tendencies manifesting themselves according to the relative concentrations of ZrO_2 and SiO_2.

CONCLUSIONS and SUMMARY

Research has been initiated on the possible production of a mixed or co-gel of hydrated silica and zirconia, by mixing sodium silicate and zirconyl chloride.

Many methods were tried for peptization or elimination of the troublesome precipitate of zirconium hydroxide. This difficulty was partly alleviated by dilution of the original silicate solution before adding it to the zirconyl chloride, but this method was good only up to certain limits.

Interesting differences in some of the physical properties and general characteristics were noted between the pure zirconia or silica and the possibly mixed gel.

It appears to me that this subject offers interesting possibilities for future research. Certain troublesome factors were in part eliminated in the course of this research, but the great portion of the work lies ahead. The following suggestions for further work are made:

1. To devise a means of more carefully controlling the conditions and pH in the case where sodium

acetate and acetic acid were used in order to make possible further investigation is this field.

2. To obtain more accurate data in an attempt to verify the necessarily rather rough initial investigations which have been made.

3. To study more carefully and more fully all the properties of the gels made and determine with more certainty when one has or has not a co-gel.

The limited time at my disposal, coupled with the very troublesome preliminary difficulties, placed a very serious restriction on the work which could be accomplished, but I am certain that conscientious work in the directions suggested above will produce interesting and fruitful results.

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